

CHEMICAL AGENT PERFORMANCE OF SULFONATED IONOMERIC MEMBRANES FOR CHEM/BIO APPLICATIONS

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ABSTRACT

The Army Research Lab (ARL) has developed a selectively permeable membrane that shows promising properties for chemical protective applications such as clothing or tenting. The flexible polymeric membrane exhibits high water vapor transport allowing reduced heat stress and barrier properties that resist penetration of chemical agents. This paper will discuss the development of this technology with a focus on the chemical agent performance, highlighting the best candidates for protective clothing applications. Current and future investigations will be discussed as well as the challenges and limitations of the current test methodology.

1. INTRODUCTION

The U.S. Army requires that all fielded systems be survivable in a chemical warfare environment. Past and presently fielded protective clothing utilizes either butyl rubber (Lee, 1990) that is not breathable or activated carbon that does breathe but is heavy and cumbersome to wear. Both designs result in fatigue and possible heat stress on the soldier. Outfitting the soldier with protective gear that is lightweight, flexible and breathable is necessary to enable the soldier to move freely in hazardous environments and therefore increases soldier survivability.

In an effort to address these multiple requirements, the Army Research Laboratory has developed a series of sulfonated tri-block copolymers (Crawford et al. 2000, Elabd et al. 2003, 2004, Harris et al., 2002, Napadensky et al., 2000, U.S. Patent 2003, 2007). The novel polymers are comprised of polyisobutylene as a major component to provide barrier properties to the block copolymer. The novel block copolymers exhibit flexibility over a broad temperature range and selectively permeable “membrane-like” characteristics. The multifunctional polymer has been shown to adhere well to woven fabric such as the battle dress uniform (BDU) and can be applied to fabric using conventional textile coating equipment.

The technologically advanced material exhibits selectively permeable properties as a result of a three phase morphology comprised of a soft rubbery hydrophobic phase (polyisobutylene), a hard polar

hydrophilic phase (sulfonated polystyrene) and ionic domains. The tri-block copolymer is referred to throughout this paper as SIBS (polystyrene-polyisobutylene-polystyrene). A schematic of the morphology of the ion-modified tri-block copolymer is shown in Figure 1. The membrane morphology and transport properties have been fully characterized and documented in the literature.²⁻¹⁰

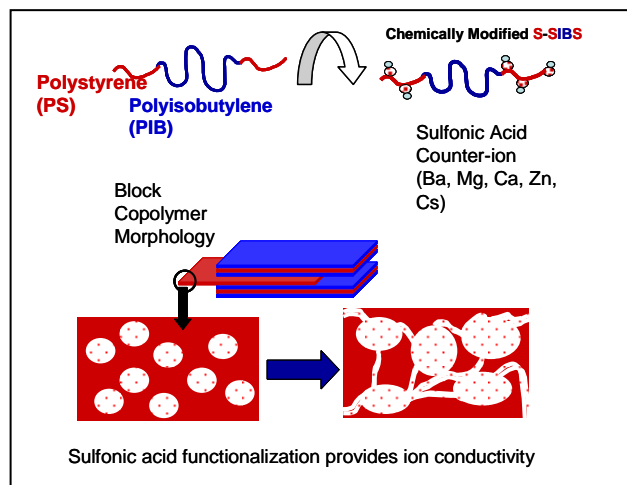


Figure 1. Morphology of ion-modified tri-block copolymer.

2. EXPERIMENTAL

2.1 Chemical Agent Tests

The focus of this paper is to present and discuss the live chemical agent tests performed on various SIBS membrane formulations. Live agent tests using both HD and GD agents were performed at Battelle Laboratories using the liquid penetration method in accordance with U.S. Army Test and Evaluation Command (ATEC) Test Operating Procedure (TOP) 8-2-501 *Permeation and Penetration Testing of Air-Permeable, Semi-Permeable, and Impermeable Materials with the Chemical Agents or Simulants (Swatch Testing)* dated March 3, 1997.

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Each sample was seal checked to ensure no leaks around the swatch before and after testing. The swatches were either pre-treated with simulated sweat treatment or preconditioned for 30 minutes at $90\pm 2^\circ\text{F}$ and $80\pm 5\%$ RH and subsequently challenged with 10 mg of mustard (HD) or soman (GD). All samples were manual spiked to ensure that none of the materials were punctured. Agent droplets were deposited evenly over the exposed 10-cm^2 area of each swatch. The number of droplets that were applied to obtain the desired 10-g/m^2 contamination density (assuming 100% purity) was eight $1\text{-}\mu\text{L}$ drops of HD ($1.27\text{ mg}/\mu\text{L} \times 8\text{ }\mu\text{L} = 10.2\text{ mg}$ total over a 10-cm^2 area) or ten $1\text{-}\mu\text{L}$ drops of GD ($1.02\text{ mg}/\mu\text{L} \times 10\text{ }\mu\text{L} = 10.2\text{ mg}$ total over a 10-cm^2 area).

The swatches were tested under dual flow conditions at $90\pm 2^\circ\text{F}$ and $80\pm 5\%$ RH for 24 hours. Sample intervals for the trial were 0-6 hours, 6-16 hours, and 16-24 hours. Samples were collected in impingers (bubblers) filled with 10 ml of Ethylene Glycol Diacetate (EGDA).

Visual observations were made of the swatches at the end of testing. Each swatch was intact, with no punctures, tears, or etchings observed. Sample analysis was performed using a gas chromatograph coupled with a flame photometric detector or a flame ionization detector (GC-FPD/FID).

2.2 Materials

Poly(styrene-isobutylene-styrene) tri-block copolymer was provided by Kuraray Co., Ltd., Tsukuba Research Laboratories with the following reported properties: 19.36 mol% (30.84 wt %) styrene, 0.95 specific gravity, $M_w=71,920\text{ g/mol}$, $M_n=48,850\text{ g/mol}$ and $\text{PDI}=1.47$. The styrene monomeric units in SIBS were sulfonated in solution to approximately 85% (mol) with methylene chloride as the solvent and acetyl sulfate as the sulfonating agent. Details of the sulfonation methods are reported elsewhere (Elabd, et al., 2003, 2004).

After sulfonation, the SIBS polymers were solvent cast from a toluene/hexanol (85/15 wt %) solution in an open teflon petri dish for several days at ambient conditions. SIBS films that have not been sulfonated were cast from pure toluene. The films were then annealed under vacuum at 50°C for an additional two weeks to remove any residual solvent.

Numerous cations were selected for substitution with the acidic hydrogen in the sulfonated styrene domains of SIBS. The

hydrogen/cation exchange was performed by immersion of the sulfonated membranes in a 1.0 M aqueous solution of the appropriate salts (magnesium perchlorate $\text{Mg}(\text{ClO}_4)_2$, calcium chloride CaCl_2 , barium chloride BaCl_2 , cesium chloride CsCl , zinc chloride ZnCl_2 , and aluminum chloride hexahydrate $\text{AlCl}_3\cdot 6(\text{H}_2\text{O})$, depending on the desired cation). The crosslinked solutions were washed with de-ionized water and left to dry for at least 24 hours in a vacuum oven at 50°C .

Hereafter, the sulfonated tri-block copolymers are referred to as SIBS-X, where X denotes either the acidic form of the sulfonated polymer (SIBS-H) or the counter ion used to substitute the acidic hydrogen (eg. SIBS-Mg).

3. RESULTS

Tables 1 and 2 show the live agent permeation results of the SIBS based membranes after exposure to live agents HD and GD respectively. For each trial, at least four and typically 5 replicate samples were evaluated. The HD live agent trial (Table 1) included films of unsulfonated SIBS in addition to the acid form of the sulfonated SIBS membrane as well as five formulations with different counter-ions. The Target Performance Value (TPV) for HD permeation is $25.84\mu\text{g}/\text{cm}^2$. The TPV is the maximum allowable concentration of HD that is allowed to permeate the membrane over a 24 hour period. The data in Table 1 show that the unsulfonated SIBS films exhibit poor barrier resistance to HD. Sulfonating the films to approximately 85% (mol) indicates a significant reduction of HD permeation in three of the five samples. However, the geometric mean (114.37) and the 95% confidence interval indicate that the permeation values are significantly higher than the TPV and widely variable.

Counter-ion substitution of the acidic hydrogen shows consistently lower HD permeation in all of the ion-modified membranes as well as significantly reduced variability. Based on the geometric mean, four of the five ion modified membranes (Al, Ba, Mg, Zn) are less than the TPV indicating passing test results. The data indicates that a significant improvement in barrier performance to live agent can be achieved by introducing ions to the sulfonated domains. The ions electrostatically bond neighboring styrene domains, enhancing domain separation and acting as non-covalent crosslinks. The ions effectively add a third domain to the complex phase separated morphology. The cation size, charge and electronegativity influence the barrier performance of the copolymer membrane to the live agent. The Ba modified membrane exhibits outstanding barrier resistance to HD, with permeation values so low that they are close to the

minimum detection limit of the instrumentation. Also notable for the Ba modified membrane is the high degree of reproducibility across the five replicate samples.

Table 1. HD Permeation After 24 Hours

Membrane Sample	HD permeation after 24 hrs $\mu\text{g}/\text{cm}^2$					Geometric Mean	95% Confidence Interval on the Geometric Mean	
Un sulfonated SIBS	324.89	325.92	275.12	265.42	223.70	280.28	230.61	340.65
SIBS-H	277.72	65.12	235.95	67.75	67.52	114.37	45.75	285.90
SIBS-Al	6.50	3.43	4.43	4.35	4.97	4.64	3.48	6.18
SIBS-Ba	1.18	0.75	0.75	1.57	0.75	0.98	0.62	1.54
SIBS-Cs	73.48	33.32	20.60	68.72	5.93	29.01	8.05	104.58
SIBS-Mg	10.75	9.79	5.82	3.85	40.78	9.92	3.28	30.04
SIBS-Zn	58.32	16.33	9.32	3.42	6.14	11.39	2.99	43.32

GD permeation results are shown in Table 2. The TPV for GD is $12.39 \mu\text{g}/\text{cm}^2$. The Ba modified membrane performed exceptionally well against the GD challenge similar to the HD trial. The data was virtually identical using both agents. Membranes using Cs, Mg and Zn cations, while generally showing an improvement of barrier resistance to GD compared to the acid form of the polymer, exhibited significantly greater variability than the same formulations tested against HD. This variability

may be attributable to the higher vapor pressure of GD and thus a faster rate of evaporation, resulting in greater variability of the volume of GD present on the samples during the test. The highly reproducible results seen with the Ba modified membrane is likely the result of the high barrier resistance of the membrane. Because virtually no GD or HD is allowed to permeate the Ba membrane, the permeation results appear highly reproducible for that formulation. High reproducibility and very low permeation was also observed in the HD testing of the Al modified membranes. Al modified membranes have not been tested for GD resistance.

Table 2. GD Permeation After 24 Hours

Membrane Sample	GD Permeation After 24 Hours $\mu\text{g}/\text{cm}^2$					Geometric Mean	95% Confidence Interval on the Geometric Mean	
Un sulfonated SIBS	NT	NT	NT	NT	NT			
SIBS-H	25.91	166.90	118.14	88.75	-	82.05	22.58	298.13
SIBS-Ba	0.75	0.75	0.75	0.75	0.75	0.75	NA	NA
SIBS-Cs	28.70	0.75	62.07	13.36	0.75	6.69	0.51	87.40
SIBS-Mg	190.31	9.09	0.75	56.42	0.75	8.87	0.40	198.08
SIBS-Zn	1.00	315.98	59.52	3.12	108.11	22.94	1.10	479.69

NT: Not Tested

NA: Not Applicable

Barium and cesium modified membranes were selected for a simulated sweat pre-treatment condition followed by HD testing. The typical field conditions for chemical protective suits are in hot climates and the nature of work while wearing the suit generates heat and perspiration. Therefore, assessing the performance of the

membrane under similar conditions is important. The membrane swatches were pre-treated with wet sweat for 60 minutes and then blotted dry prior to assembly in the test cell. HD permeation of Ba and Cs membranes before and after simulated sweat pre-treatment is shown in Table 3. The data clearly show that the Ba modified membranes

lose barrier resistance to HD and exhibit poor reproducibility following sweat pre-treatment. Although further work will need to be performed to determine the reason for reduced agent resistance, it is speculated that once the membranes are saturated with the aqueous salt solution, swelling in the material may cause a rearrangement of morphology resulting in less order or packing in the chemical structure allowing permeation of the HD agent. Interestingly, the Cs modified membrane did not exhibit a change before or after the simulated sweat pre-treatment, however, the TPV for Cs exceeds the allowable amount of HD permeation in either case. Cs and Ba are very similar in size but differ in cation charge (Cs^{+1} , Ba^{+2}). Thus, Cs can only bond with one oxygen of

the sulfonate group while Ba can theoretically bond with two sulfonate oxygen's. Bonding more than one oxygen may result in better packing in the membrane prior to sweat pretreatment and therefore improved barrier properties as observed with Ba (and Al^{+3}), however, multiple bonds of a multi-valent cation may be more labile under wet conditions than the monovalent Cs cation, resulting in a reduction of barrier resistance following the sweat pre-treatment. Further testing with additional di and tri-valent cations will be necessary to better understand the effect of wet treatment on the barrier performance of the membranes.

Table 3. HD Permeation Before and After Simulated Sweat Pre-treatment

Membrane Sample	HD Permeation After 24 Hours $\mu\text{g}/\text{cm}^2$				Geometric Mean	95% Confidence Interval on the Geometric Mean	
No Pre-treatment SIBS-Ba	0.75	0.75	0.75	1.40	0.88	0.53	1.45
Simulated Sweat Pre-treatment SIBS-Ba	86.19	3.06	46.02	5.45	16.05	1.23	210.12
No Pre-treatment SIBS-Cs	29.39	22.50	56.66	58.06	38.41	18.01	81.88
Simulated Sweat Pre-treatment SIBS-Cs	39.05	23.89	53.20	36.27	36.63	21.67	61.90

CONCLUSIONS

We have investigated the chemical agent resistance of a series of novel tri-block copolymer membranes developed at the Army Research laboratory. These membranes are lightweight, flexible and exhibit high water vapor permeation making them candidate materials for breathable clothing applications. A series of these membranes were evaluated for live chemical agent performance. The results reveal that chemically modifying the sulfonated SIBS polymers with cations is necessary to achieve barrier resistance to agents HD and GD. The cations varied in size, charge and electronegativity.

The barium modified membranes exhibited outstanding barrier performance with breakthrough

values so low that they approached the minimum detection levels of the Battelle instrumentation against both HD and GD challenges. The exceptionally low permeation observed for the Ba modified membranes also resulted in excellent reproducibility for these membranes compared to the other cations. Similar results were also observed for the Al modified membranes with HD permeation. GD permeation has not been performed on the Al modified membranes. Because of the excellent resistance of the Ba modified membranes to both HD and GD, it was surprising to see that these properties were diminished somewhat following the simulated sweat pre-treatment. We speculate that the difference in performance of the Ba and Cs modified membranes before and after simulated sweat treatment may be a result of the difference in charge of these two cations and their ability to interact with only one sulfonated oxygen in the case of Cs and two sulfonate oxygens in the case

of Ba. While the divalency of Ba may result in a greater ionic “crosslinking” effect in the dry state, these interactions may be weaker and more labile when exposed to the 60 minute sweat pre-treatment resulting in a loss of barrier resistance following the treatment.

Future work would entail simulated sweat pre-treatment testing on other mono and multi-valent cations to determine if there is a trend in multivalent cation modified membranes to show decreased barrier resistance following exposure to aqueous salt solution. The decrease in barrier performance of these membranes following sweat treatment, although notable, is within reasonable limits for further optimization.

The exceptional barrier resistance of the Ba modified membranes and potentially the Al modified membranes against live chemical agents is truly impressive for flexible polymer films. These properties combined with the high level of water vapor permeation necessary for removing perspiration from the wearer make these polymers excellent candidates for further development for chemical protective fabric applications.

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